b) Polymerization

The polymerization was carried out in a reactor having an output of 50 kg/h of polyethylene. As can be seen from table 1, the reactor was started up at an MFR increased over that under production conditions over a start-up period of 15 hours by operating it at the beginning at an increased ratio of the flow of hydrogen to the flow of ethylene compared to long-term operation. A polymerization product having an MFR (190°C/2.16 kg) of above 15 g/10 min was produced at the beginning and the MFR was reduced to the desired value of below 4 g/10 min over a period of about 15 hours.

In addition, the reactor temperature was initially set to 97°C and after the polymerization reaction had started (about 2 hours) was reduced to the production temperature of 95°C.

The start-up phase and the subsequent production operation were stable with a small amount of material being discharged from the circulated gas cyclone. The formation of lumps was not observed.

Table 1

Time	Reactor pressure	Reactor temp.	Circulated gas	Nitrogen	Ethene	Hexane	Hexene	H_2 to reactor	Ethene to reactor	Hexene to reactor	Offgas from reactor	Catalyst	Fines	Lumps	MFR	Density	Bulk density
h	bar	°C	m³/h	vol%	vol%	vol%	vol%	l/h	kg/h	kg/h	kg/h	g/h	g/3h	g/h	g/10 min	g/cm³	g/l
0	20.0	97.1	300	38.8	58.2	2.33	1.40	29.8	10.1	1.10	15.00	12.57	8				
1	20.1	97.1	300	38.3	58.2	2.76	1.52	29.8	8.7	0.92	14.89	6.58					
2	20.0	96.2	300	42.6	53.8	2.87	1.53	29.8	8.2	0.88	12.06	5.68					
3	20.0	95.4	300	43.9	52.6	2.82	1.46	29.8	15.0	0.93	10.02	6.28	3				
4	20.0	95.2	300	43.9	52.8	2.62	1.28	29.8	16.2	1.33	10.01	6.58					
5	20.0	95.1	300	45.4	51.5	2.47	1.22	29.8	18.6	1.82	10.00	6.88					
6	20.0	95.1	300	46.0	51.0	2.39	1.26	29.8	21.6	2.24	10.00	7.18	1				
7	20.0	95.1	300	46.1	50.9	2.37	1.31	29.8	24.9	2.52	9.99	7.78			15.6	0.9202	465
8	20.0	95.0	307	45.8	51.1	2.39	1.34	29.8	26.8	2.72	10.00	.,78					
9	20.0	95.0	327	45.2	51.6	2.42	1.39	29.8	28.7	3.12	9.68	8.08	2		11.1	0.9224	450
10	20.0	95.0	347	45.2	51.4	2.45	1.46	29.8	26.2	2.88	6.54	8.08					

Time	Reactor pressure	Reactor temp.	Circulated gas	Nitrogen	Ethene	Hexane	Hexene	H_2 to reactor	Ethene to reactor	Hexene to reactor	Offgas from reactor	Catalyst	Fines	Lumps	MFR	Density	Bulk density
h	bar	°C	m³/h	vol%	vol%	vol%	vol%	l/h	kg/h	kg/h	kg/h	g/h	g/3h	g/h	g/10 min	g/cm³	g/l
11	20.0	95.0	367	46.7	49.9	2.50	1.44	29.8	26.4	2.90	5.98	8.68			9.72	0.9202	480
12	20.0	95.0	380	46.9	49.7	2.52	1.44	29.8	28.2	3.10	5.99	8.68	8				
13	20.0	95.1	380	46.1	50.5	2.52	1.47	29.8	29.7	3.27	5.99	9.27			8.60	0.9201	485
14	20.0	95.0	380	44.9	51.7	2.48	1.52	29.8	32.3	3.54	5.97	9.27					
15	20.0	95.1	380	43.6	52.9	2.44	1.58	29.8	34.6	3.79	5.98	9.87	13		7.59	0.9199	496
16	20.0	95.1	380	42.4	54.1	2.41	1.61	29.8	36.1	3.94	6.00	10.17					
17	20.0	95.1	380	41.4	55.2	2.42	1.60	29.8	37.8	4.15	5.98	10.47			5.72	0.9196	499
18	20.0	95.0	380	40.8	55.8	2.43	1.64	29.8	38.2	4.20	6.00	10.77	25				
19	20.0	95.1	380	40.9	55.7	2.44	1.65	29.8	39.0	4.29	6.01	11.07			5.34	0.9191	495
20	20.0	95.0	380	41.2	55.4	2.44	1.65	29.8	39.1	4.30	5.99	11.67					
21	20.0	95.0	380	41.7	54.9	2.47	1.63	29.8	39.5	4.35	6.00	11.97	23		4.55	0.9192	502
22	20.0	95.0	380	42.3	54.3	2.51	1.60	29.8	40.2	4.42	6.01	12.27					
23	20.0	95.0	380	43.0	53.6	2.54	1.57	29.8	41.0	4.51	5.99	13.46			4.31	0.9191	506
24	20.0	95.0	380	44.7	52.0	2.52	1.52	29.8	40.4	4.44	6.01	14.06	40				
25	20.0	95.0	380	46.2	50.5	2.54	1.46	29.8	41.2	4.53	6.01	14.66			4.40	0.9192	440
26	20.0	95.0	380	46.8	50.0	2.48	1.45	29.0	40.7	4.48	6.01	14.66					
27	20.0	95.0	380	46.7	50.1	2.50	1.45	27.8	41.4	4.60	6.01	14.36	46		4.49	0.9191	504
28	20.0	95.0	380	46.3	50.5	2.47	1.51	27.8	41.6	4.98	5.98	14.66					
29	20.0	95.0	380	45.8	50.8	2.47	1.55	27.8	42.5	5.09	5.99	14.66			4.10	0.9191	504
30	20.0	95.0	380	45.1	51.4	2.47	1.60	27.8	44.4	5.30	5.99	14.66	48				
31	20.0	95.0	380	44.1	52.4	2.47	1.61	27.8	45.2	5.41	5.98	14.36			3.85	0.9186	497
32	20.0	95.0	380	43.3	53.2	2.44	1.66	27.8	46.1	5.52	6.03	14.66					
33	20.0	95.0	380	42.4	54.0	2.47	1.67	27.8	46.6	5.56	5.95	14.66	55		3.59	0.9188	512
34	20.0	95.0	380	41.9	54.4	2.45	1.70	27.8	46.9	5.62	5.95	14.36					
35	20.0	95.0	380	41.4	54.9	2.47	1.72	27.8	47.9	5.75	5.98	14.66			3.43	0.9187	510
36	20.0	95.0	380	41.1	55.3	2.48	1.73	27.8	48.2	5.77	5.99	14.66	51				
37	20.0	95.0	380	40.8	55.5	2.48	1.74	27.8	47.8	5.74	6.01	14.36			3.18	0.9187	514
38	20.0	95.0	380	40.8	55.6	2.51	1.74	27.8	48.7	5.84	5.98	14.66					
39	20.0	95.0	380	40.8	55.5	2.48	1.75	29.6	48.4	5.80	5.98	14.66	57		3.27	0.9187	506

Comparative example 1

a) Preparation of the supported catalyst

105.4 g of bis(1-methyl-3-butylcyclopentadienyl)zirconium dichloride were dissolved in 6.4 l of methylaluminoxane (MAO, Albemarle, 30% in toluene) and the mixture was stirred for one hour at room temperature. The solution was added slowly while stirring to 4.5 kg of silica gel (Ineos ES70X), which had previously been calcined at 600°C for 6 hours, with the temperature being kept below 40°C. After the addition was complete, 0.5 l of toluene was added to rinse out the flask containing the MAO/bis(1-methyl-3-butylcyclopentadienyl)zirconium dichloride solution. The catalyst was dried under reduced pressure to give a free-flowing powder.

The catalyst contained 31% by weight of volatile substances and had an elemental composition of 8.3% by weight of aluminum and 0.21% by weight of zirconium.

b) Polymerization

The polymerization was carried out in a reactor having an output of 6.5 kg/h of polyethylene. As can be seen from table 2, a polymerization product having an MFR (190°C/2.16 kg) of below 4 g/10 min was produced in the reactor from the beginning by introducing a significantly smaller, compared to example 1, hydrogen flow relative to ethylene into the reactor.

After only one hour of operation, lumps were evident in the reactor and finally led, after about 21 hours, to shutdown of the reactor since the product discharge opening had become blocked.

Table 2

Time	Reactor pressure	Reactor temp.	Circulated gas	Nitrogen	Ethene	Hexane	Hexene	H_2 to reactor	Ethene to reactor	Hexene to reactor	Offgas from reactor	Catalyst	Fines from CGC	Lumps	MFR	Density	Bulk density
h	bar	°C	m³/h	vol%	vol%	vol%	vol%	l/h	kg/h	kg/h	kg/h	g/h	g/3h	g/h	g/10 min	g/cm³	g/l
0	20.0	95.0	38	41.9	54.8	2.97	1.37	0.49	1.1	105.5	1.2	1.03					
1	20.0	95.0	38	41.2	55.2	3.18	1.41	0.49	1.1	102.1	1.2	0.95	6				
2	20.0	95.0	38	41.2	55.3	3.08	1.42	0.49	1.1	96.8	1.2	0.95					
3	20.0	95.0	38	41.6	55.0	3.01	1.41	0.49	1.1	94.8	1.2	0.95					

Time	Reactor pressure	Reactor temp.	Circulated gas	Nitrogen	Ethene	Hexane	Hexene	H_2 to reactor	Ethene to reactor	Hexene to reactor	Offgas from reactor	Catalyst	Fines from CGC	Lumps	MFR	Density	Bulk density
h	bar	°C	m³/h	vol%	vol%	vol%	vol%	l/h	kg/h	kg/h	kg/h	g/h	g/3h	g/h	g/10 min	g/cm³	g/l
4	20.0	94.9	38	41.2	55.4	2.98	1.39	0.49	1.2	97.2	1.2	0.27	6				
5	20.0	95.0	38	39.5	57.1	3.00	1.43	0.49	1.1	91.1	1.2	0.11					
6	20.0	95.0	38	39.9	56.7	3.00	1.43	0.49	0.9	83.8	1.2	0.11					
7	20.0	95.1	38	42.2	54.5	2.98	1.41	0.49	0.8	81.4	1.2	0.71	5				
8	20.0	95.0	38	45.8	51.1	3.00	1.35	0.49	1.1	92.9	1.2	0.95					
9	20.0	95.1	38	45.2	51.6	3.01	1.31	0.49	1.5	112.5	1.2	1.01					
10	20.0	95.1	38	42.9	54.0	2.96	1.29	0.49	1.8	134.6	1.2	1.05	2				
11	20.0	95.1	38	41.1	55.8	2.96	1.28	0.49	2.1	158.2	1.2	1.11		15			
12	20.0	95.1	38	40.8	56.1	2.96	1.24	0.49	2.4	188.9	1.2	1.18		6			
13	20.0	95.1	38	41.1	55.8	3.00	1.22	0.49	2.8	225.5	1.2	1.16	1	9			
14	20.0	95.1	38	41.7	55.1	3.01	1.25	0.49	3.1	281.3	1.2	1.16		6			
15	20.0	95.1	39	42.0	54.9	2.94	1.30	0.49	3.4	309.6	1.2	1.18		8			
16	20.0	95.1	41	42.0	54.8	2.97	1.32	0.49	3.7	323.4	1.2	1.24	10	8			
17	20.0	95.1	41	42.3	54.5	2.98	1.30	0.49	4.1	341.5	1.2	1.24		8			
18	20.0	95.2	41	42.3	54.5	2.95	1.28	0.49	4.3	357.4	1.1	1.34		11	2.58	0.9211	384
19	19.9	95.3	41	43.9	53.0	2.94	1.23	0.49	5.0	420.1	0.8	1.37	68	15			
20	20.1	95.1	41	42.4	54.5	2.92	1.24	0.49	4.5	469.1	0.7	0.86	38	12	1.94	0.9210	408
21	18.8	83.9	34	43.8	51.7	2.92	1.38	0.13	1.3	162.9	1.9						
22	1.2	60.6	3	38.0	13.8	3.10	1.29			0.0	0.4						
23		60.0		2.33	0.03	4.21	1.64			0.0							

Example 2

a) Preparation of the supported catalyst

4 kg of silica gel (Grace Davison XPO2107) was calcined at 600°C for six hours, subsequently suspended in 20 l of toluene and cooled to 10°C. 9.61 l of methylaluminoxane (MAO, Albemarle, 30% in toluene) were slowly added while stirring, with the temperature being kept below 12°C. A further 1.2 l of toluene were added and the temperature of the flask was increased to 25°C. The

Table 3

Time	Reactor pressure	Reactor temp.	Circulated gas	Nitrogen	Ethene	Hexane	Hexene	H_2 to reactor	Ethene to reactor	Hexene to reactor	Offgas from reactor	Catalyst	Fines from CGC	Lumps	MFR	Density	Bulk density
h	bar	°C	m³/h	vol%	vol%	vol%	vol%	l/h	kg/h	kg/h	kg/h	g/h	g/3h	g/h	g/10 min	g/cm³	g/l
0	20.0	97.1	300.	40.0	56.8	2.76	1.64	29.8	14.4	0.70	15.00	12.57					
1	20.0	96.9	300.	35.7	61.4	2.56	1.55	29.8	11.8	0.62	13.48	5.98	3				
2	20.0	95.9	311.	37.4	59.9	2.47	1.40	29.8	15.2	1.04	10.18	5.68					
3	20.0	95.2	320.	38.1	59.3	2.43	1.36	29.8	19.3	1.74	10.00	5.98					
4	20.0	95.2	320.	39.6	57.8	2.47	1.36	29.8	23.9	2.07	10.01	6.58	2				
5	20.0	95.1	329.	41.0	56.4	2.44	1.36	29.8	26.8	2.65	10.00	7.18					
6	20.0	95.1	340.	42.5	54.9	2.37	1.47	29.8	29.5	3.22	9.87	7.78					
7	20.0	95.0	354.	44.4	53.0	2.25	1.51	29.8	27.5	3.03	6.30	8.98	1		8.69		458
8	20.0	95.1	371.	47.1	50.5	2.21	1.49	29.8	32.4	3.56	5.97	9.57					
9	20.0	95.1	380.	46.5	51.2	2.04	1.52	29.8	36.1	3.94	5.98	9.87			8.8	0.9227	470
10	20.0	95.1	380.	44.9	52.8	1.92	1.58	29.8	38.4	4.17	5.98	10.17	5				
11	20.0	95.1	380.	43.6	54.2	1.86	1.64	29.8	42.0	4.62	5.98	10.77			7.3	0.9223	485
12	20.0	95.0	380.	42.6	55.1	1.87	1.70	29.8	42.9	4.73	5.98	11.07					
13	20.0	95.1	380.	42.0	55.7	1.89	1.72	29.8	45.1	4.93	5.99	11.37	13		3.1	0.9221	490
14	20.0	95.0	380.	41.7	55.9	1.92	1.76	29.8	45.5	5.01	5.99	11.37					
15	20.0	95.1	380.	42.2	55.4	1.92	1.77	34.4	45.6	5.01	5.99	11.37			5.6	0.9205	500
16	20.0	95.0	380.	42.7	54.8	1.94	1.77	38.4	47.5	5.24	5.99	11.37	20				
17	20.0	95.0	380.	42.8	54.7	1.94	1.77	35.4	46.7	5.14	5.99	11.67			5.1	0.9203	504
18	20.0	95.1	380.	43.0	54.6	1.99	1.76	33.4	46.9	5.17	5.99	12.27					
19	20.0	95.0	380.	43.1	54.4	2.02	1.76	33.3	47.6	5.25	5.99	12.27	5		6.4	0.9194	501
20	20.0	95.0	380.	43.2	54.3	1.99	1.75	33.3	47.9	5.27	5.99	12.27					
21	20.0	94.9	380.	43.2	54.3	2.02	1.74	29.9	46.4	5.12	5.98	12.27			6.3	0.9201	509
22	20.0	95.1	380.	43.2	54.3	2.01	1.79	29.4	46.8	5.14	5.99	12.27	16				
23	20.0	95.0	380.	43.2	54.3	2.02	1.77	29.7	47.8	5.27	6.01	11.97			5.84	0.9183	500
24	20.0	95.0	380.	43.2	54.4	1.98	1.76	29.4	46.7	5.14	6.01	11.37					
25	20.0	95.0	380.	43.2	54.4	1.96	1.68	28.8	45.6	5.02	5.99	11.67	27		4.42	0.9194	502
26	20.0	95.0	380.	43.2	54.3	1.93	1.65	28.7	45.4	5.00	6.00	11.67					
27	20.0	95.0	380.	43.3	54.2	2.00	1.67	29.0	45.9	5.05	6.01	11.67			3.94	0.9195	497
28	20.0	95.0	380.	43.2	54.3	2.02	1.66	28.7	45.4	5.00	6.00	11.67	39	7			

Time	Reactor pressure	Reactor temp.	Circulated gas	Nitrogen	Ethene	Hexane	Hexene	H_2 to reactor	Ethene to reactor	Hexene to reactor	Offgas from reactor	Catalyst	Fines from CGC	Lumps	MFR	Density	Bulk density
h	bar	°C	m³/h	vol%	vol%	vol%	vol%	l/h	kg/h	kg/h	kg/h	g/h	g/3h	g/h	g/10 min	g/cm³	g/l
29	20.0	95.0	380.	43.2	54.3	2.04	1.65	28.9	45.8	5.04	6.03	11.67			3.92	0.9181	495
30	20.0	95.0	380.	43.1	54.3	2.07	1.67	28.7	45.5	5.00	5.98	11.67					
31	20.0	95.0	380.	43.1	54.4	1.98	1.70	28.6	45.4	5.00	5.96	11.67	50		3.79	0.9193	501
32	20.0	95.0	380.	43.4	54.0	1.98	1.67	28.8	45.7	5.03	5.99	11.97					
33	20.0	95.0	380.	43.5	54.0	1.94	1.69	28.6	45.3	4.99	5.99	11.67			3.71	0.9192	501
34	20.0	95.0	380.	43.2	54.3	1.87	1.65	29.4	46.7	5.15	5.99	11.67	66				
35	20.0	95.0	380.	42.9	54.7	1.90	1.65	29.4	46.7	5.14	6.00	11.67			3.75	0.9186	492
36	20.0	95.0	380.	42.6	54.9	1.94	1.60	29.3	46.6	5.14	6.00	11.67					
37	20.0	95.0	380.	42.3	55.2	2.07	1.65	29.2	46.7	5.14	6.01	11.67	76		3.68	0.9187	497

Example 3

a) Preparation of the supported catalyst

4 kg of silica gel (Grace Davison XPO2408, particle diameter about 45 µm) was calcined at 600°C for six hours, subsequently suspended in 20 l of toluene and cooled to 10°C. 9.61 l of methylaluminoxane (MAO, Albemarle, 30% in toluene) were slowly added while stirring, with the temperature being kept below 12°C. A further 1.2 l of toluene were added and the temperature of the flask was increased to 25°C. The silica gel/MAO suspension was filtered, the solid was resuspended in 30 l of toluene, stirred for 15 minutes and filtered again. This purification step was repeated twice more.

The moist silica gel/MAO was suspended in 20 l of toluene at 25°C. 60.5 g of bis(1-methyl-3-butylcyclopentadienyl)zirconium dichloride were dissolved in 0.75 l of toluene and added to the silica gel/MAO suspension while stirring. After the addition was complete, the mixture was stirred for another 2 hours. The suspension was filtered, the solid was resuspended in 20 l of toluene, filtered again and dried at 50°C under reduced pressure to give a free-flowing catalyst powder.